

## BRIEF COMMUNICATION

# Reply to “Does Lanthanide Substitution Reduce Titanium from $Ti^{4+}$ to $Ti^{3+}$ in the Perovskite $CaTiO_3$ Fired at $1550^\circ C$ in Air?”

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Dadachov (1) asserts that “compounds with formulae  $Ca_{0.85}Gd_{0.15}TiO_3$  and  $Ca_{0.925}Gd_{0.075}TiO_3$  do not exist.” In reaching this conclusion, he ignores the direct evidence from microanalysis that, after firing in air, the  $Ca_{1-x}Gd_xTiO_3$  ( $x < 0.18$ ) series does exist. He notes that “the accuracy of EDS microanalysis is well known,” but it is clear that he himself is not aware of the accuracy that can be achieved with EDS microanalysis. We have given a detailed description of our general analytical methods (2). The original analytical data are true absolute values, not simply normalized ratios, and were based on detailed calibrations. Inspection of Fig. 1 of our paper shows that for a given grain in  $Ca_{1-x}Gd_xTiO_3$  the sum of Ca + Gd divided by Ti, in terms of formula units, was almost always within 2% of unity, and repeat measurements on the same grain agreed at this level of accuracy. The variation of up to 20% in composition of individual grains from the nominal composition is a true variation between localized portions of the samples. It is not a measure of the accuracy of measurement. Note also that in the series of specimens with nominal compositions  $Ca_{1-3x/2}Gd_xTiO_3$ , microanalysis indicated a Ca-vacancy concentration that would exactly compensate for the number of  $Gd^{3+}$  ions present, assuming that all Ti was in the form  $Ti^{4+}$ . This is further confirmation of the accuracy of our microanalysis.

Dadachov is also unaware of the significance of our X-ray observations (2). What they show is that in the series of samples where microanalysis indicated the presence of vacancies (Fig. 2 (2)), the unit cell volume decreased with increasing Gd content, whereas in those samples where no vacancies were detected by microanalysis (Fig. 1 (2)), the unit cell volume increased with increasing Gd content. This is not direct evidence for the presence of  $Ti^{3+}$ , but it is very strong evidence that the composition of a grain is not dictated solely by the Gd content.

With regard to the XPS data, we maintain that our analytical procedure is the correct one, since the local environment of  $Ti^{4+}$  ions in  $Ca_{0.85}Gd_{0.15}TiO_3$  is essentially the

same as that in  $CaTiO_3$ ; therefore, it is appropriate to use the same fitting parameters to fit the  $Ti^{4+}$  peaks in the XPS spectra of the two samples. The fitting parameters (peak positions, full widths at half-maxima, and pseudo-Voigt mixing parameter) were obtained by fitting the spectrum from  $CaTiO_3$ , and the same parameters were then used for fitting the spectrum from  $Ca_{0.85}Gd_{0.15}TiO_3$ . When this was done there was a small but significant residual shoulder on the lower binding energy side of the  $Ti^{4+} 2p_{3/2}$  XPS peak, in the position expected for a  $Ti^{3+} 2p_{3/2}$  peak. Whether or not the peaks could have been fitted by a simple Lorentzian, as Dadachov asserts but does not demonstrate, it would make no sense to use different functions for doped and undoped specimens; to state that the data do not show any indication of  $Ti^{3+}$  is incorrect. It is true that the fit in the “valley” region of Fig. 4 (2) is not ideal. Had we chosen a more sophisticated background correction function than a linear one, the fit would have been improved, but we concentrated on the low binding energy “tail” region where the  $Ti^{3+} 2p_{3/2}$  peak is located, because we were only looking for a  $Ti^{3+}$  component.

We admit that there is little evidence for  $Ti^{3+}$  in  $Ca_{1-x}Gd_xTiO_3$  fired in air from XANES, cathodoluminescence, and density measurements, but Dadachov equates absence of proof with proof of absence. The XANES spectra from  $CaTiO_3$  and  $Ca_{0.85}Gd_{0.15}TiO_3$  shown in Fig. 5 (2) are clearly not identical; so, although we did not attempt to interpret the curves in detail (for reasons given), it is not possible to deduce from this evidence that  $Ti^{3+}$  is not present. The cathodoluminescence results were negative, but before one can deduce from this that  $Ti^{3+}$  was not present, it is necessary to show that, had it been present, the results would have been positive. We gave an example of a specimen where  $Ti^{3+}$  was known to be present, yet no cathodoluminescence was seen, which shows that, perhaps, our equipment was not sufficiently sensitive. We quoted no results for density measurements. Obviously, with no results one cannot draw any conclusions. We hold our view that

the evidence from these experiments is inconclusive and deny that it directly contradicts our conclusions.

We agree with Dadachov that  $\text{Ca}_{0.85}\text{Gd}_{0.15}\text{TiO}_3$  would not exist if all the Ca were present as  $\text{Ca}^{2+}$ , all the Gd as  $\text{Gd}^{3+}$ , all the Ti as  $\text{Ti}^{4+}$ , and all the O as  $\text{O}^{2-}$ , but we contend that we have shown that the compound does exist. The most probable interpretation, in the light of the available evidence, is that some of the Ti is present as  $\text{Ti}^{3+}$ , but we cannot make any explicit comment on the electronic

structure of this ion in  $\text{Ca}_{1-x}\text{Gd}_x\text{TiO}_3$  fired in air until further results on, for instance, electron paramagnetic resonance, are available.

#### REFERENCES

1. M. S. Dadachov, *J. Solid State Chem.*, preceding paper.
2. E. R. Vance, R. A. Day, Z. Zhang, B. D. Begg, C. J. Ball, and M. G. Blackford, *J. Solid State Chem.* **124**, 77 (1996).